



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB89/00535 <b>(22) International Filing Date:</b> 17 May 1989 (17.05.89)  <b>(30) Priority data:</b> 8811634.8 17 May 1988 (17.05.88) GB  <b>(71) Applicants (for all designated States except US):</b> SWIFT ADHESIVES LIMITED [GB/GB]; St. George's House, Church Street, Twickenham, Middlesex TW1 3NE (GB). AEI CABLES LIMITED [GB/GB]; Crete Hall Road, Northfleet, Gravesend, Kent DA11 9DA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> MARTIN, Leslie, Philip [GB/GB]; 15A Wordsworth Avenue, Greenford, Middlesex UB6 9AA (GB). BEVERIDGE, Colin [GB/GB]; 19 Hillingdon Road, Gravesend, Kent DA11 7LQ (GB).		<b>(74) Agents:</b> COCKBAIN, Julian, R., M. et al.; Frank B. Dehn & Co., Imperial House, 15/19 Kingsway, London WC2B 6UZ (GB).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ADHESIVE COMPOSITIONS  <b>(57) Abstract</b>  There are described hot-melt adhesive compositions containing silane-grafted polymers, especially $\alpha$ -olefin homo- or copolymers, suited to use in, for example, product assembly.		

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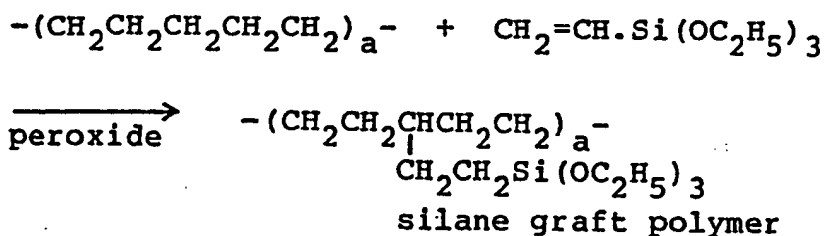
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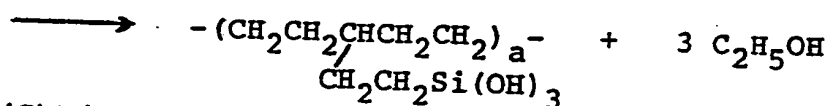
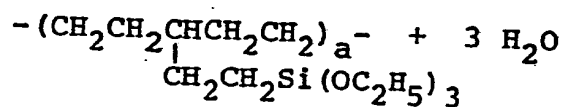
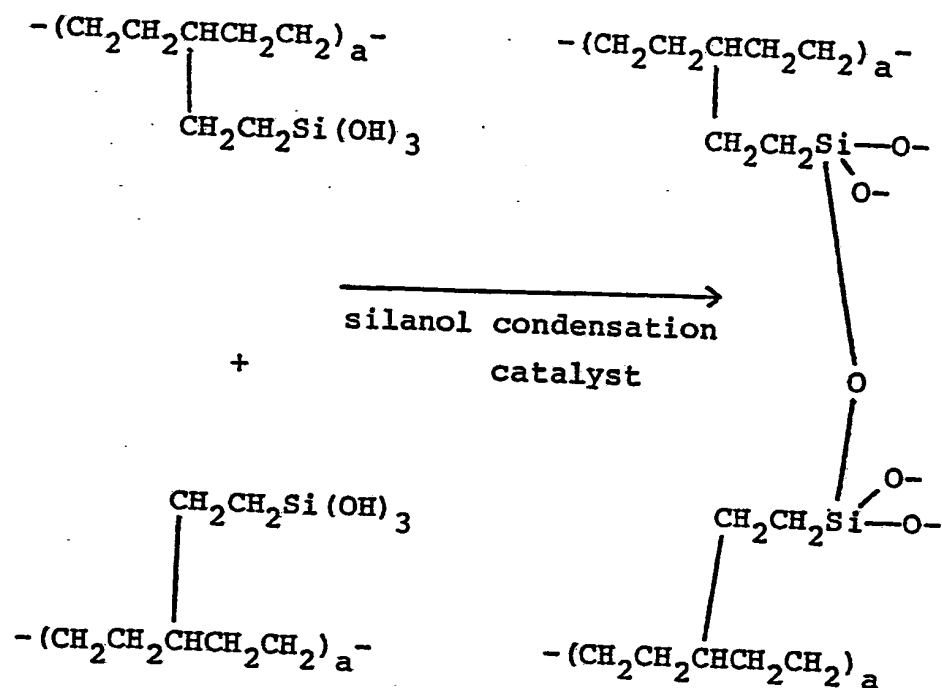
ADHESIVE COMPOSITIONS

The present invention relates to adhesive compositions, in particular to hot melt adhesive compositions comprising cross-linkable silane-modified polymers of apolar monomers.

Silane grafted homo- and co-polymers are widely used for the preparation of cable jacketing, wire insulation and piping and have been suggested for use as spacers in laminate materials. The preparation of such materials is described in for example US-A-3646155, GB-A-1286460, GB-A-1347426, GB-A-1406680, GB-A-1450934 and GB-A-1542543. US-A-3646155, for example, describes the production of such material by reaction of polyethylene with an unsaturated silane, e.g. vinyl triethoxysilane, in the presence of a peroxide initiator to produce the silane grafted polymer. A catalyst, for example dibutyl tin dilaurate, is incorporated into the grafted polymer which is then formed into the desired shape. Catalysed hydrolysis and cross-linking of the silane groups occurs to give the hardened end product. The reaction procedure may thus be represented as follows:-

(A) Grafting

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(B) Hydrolysis(C) Cross-linking

The product of stage (A) above may also be produced by copolymerisation of ethylene with a suitable trialkoxysilyl monomer, e.g. 4-(triethoxysilyl)-but-1-ene. References hereinafter to silane-grafted or silane-modified polymers include such silane side chain materials produced by copolymerisation, which are indistinguishable from the materials produced by grafting.

While teaching that for storage stability the silanol condensation catalyst should be incorporated into the silane-grafted polymer only when initiation of the cross-linking reaction is desired, Dow Corning Limited have suggested in GB-A-1406680 that silane grafted ethylene-vinyl acetate copolymers may find

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utility in adhesives. In British patent application No. 8724865 (GB-A-2197326) Swift Adhesives Limited have however suggested the use of a silane-grafted medium range molecular weight ethylene-vinyl acetate copolymer as the base for cross-linkable hot melt adhesive systems (which can either be formulated as single compositions containing the grafted copolymer together with the condensation catalyst or as dual compositions, one containing the grafted copolymer and the other the catalyst) which are particularly suitable for use in product assembly, for example in the furniture and automobile industries.

The present invention is based on the recognition that cross-linkable hot melt adhesive systems, especially single composition systems, having advantageous properties relative to adhesives based on silane-modified ethylene-vinyl acetate copolymers in terms of solvent resistance, creep resistance, flexibility, adhesion (especially to non-polar substrates such as plastics, and in particular polyolefins such as polythene, polypropylene, PTFE, etc.) and thermal stability, may be produced by the use of silane-modified homopolymers and copolymers deriving from apolar monomers and comonomers or of blends of such modified homo- or copolymers.

According to one aspect of the present invention therefore we provide an adhesive composition applicable in melt form to surfaces to be bonded, said composition comprising

- (a) at least one silane modified, including silane-grafted polymer (hereinafter collectively SGP) of apolar monomers,
- (b) a catalyst for the condensation of said silane-modified polymer, and, optionally but preferably,
- (c) a plasticizer, preferably a polybutene, polyterpene or liquid hydrocarbon plasticizer.

As it is found that the incorporation of a plasticizer into the adhesive system improves

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substrate wetting by the hot melt as well as providing improved flexibility in the cured adhesive it is particularly preferred that the adhesive system should comprise at least one plasticizer, such as for example an ester-based plasticizer (e.g. benzoate plasticizers such as glycol dibenzoate and dipropylene glycol dibenzoate (available as Benzoflex 9-88)) or a liquid polyterpene or liquid hydrocarbon plasticizer (such as for example the polyterpene available from Goodyear under the trade name Wingtack 10 and the liquid hydrogen available from Exxon under the trade name Escorez 5000) or a polybutene plasticizer. The plasticizer conveniently constitutes 5 to 40%, preferably 10-35%, of the adhesive composition.

The SGPs used according to the present invention are, as mentioned above, silane-grafted polymers of apolar monomers or comonomers, or copolymers of a silane monomer with such apolar monomers. Examples of apolar monomers include for example olefins, especially alpha-olefins and particularly C<sub>2-6</sub> alpha-olefins, (e.g. ethylene, propylene, but-1-ene, and 2-methyl-prop-1-ene), and styrenes. The polymers which are silane-modified may be homo or copolymers and if copolymers may derive from two or more different comonomers. Thus for example particular mention may be made of SEBS (styrene-ethylene-butylene-styrene), ethylene-propylene, ethylene-but-1-ene and ethylene-hex-1-ene as copolymers. Mention may also be made of EPDM (unsaturated ethylene-propylene terpolymer). Preferably however the polymer or polymer blend which is silane modified will comprise at least one polypropylene and particularly preferably it will comprise a blend of polypropylenes having molecular weights within different ranges, e.g. atactic polypropylene. Particularly conveniently the polymer blend comprises a homo- or copolymer the monomers for which are olefins such as the

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straight chained or branched unsubstituted olefins mentioned above. In this regard it may be noted that silane-grafted polyethylenes have recently (Summer 1988) become available commercially from AC Polythenes under the trade name ACX.

As mentioned above, the adhesive composition may contain one or more than one SGP. Where a blend of SGPs is used, it is particularly preferred that for each the silane side chain should be the same and it is also especially preferred that the SGPs used in preparing the composition should be polymers derived only from apolar (co)monomers. In this way compositions having optimum adhesion characteristics for plastic substrates can be produced.

Where the silane side chains are introduced by grafting this may of course be effected either before or after the polymers are blended.

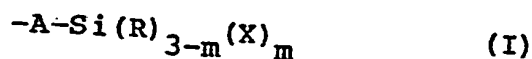
Polymers having a wide range of molecular weights may be silane grafted to produce the SGPs used for the preparation of the adhesive compositions of the present invention; in general polymers having melt flow indices (MFIs) of from 1 to 2500 may be used and MFIs of 2-1000, especially 5-400 and particularly 10-150, are preferred. By blending polymers having different pre silane grafting MFIs and indeed by blending grafted polymers having different monomer make-up (e.g. by blending silane-modified polypropylene with silane-modified polyethylene) the performance profile of the final adhesive system, for example in terms of wetting, strength, adhesion, flexibility, and ease of application, may be adjusted to suit its intended end use.

Thus in one embodiment the adhesive composition of the invention contains a blend of silane-grafted polymers for at least one of which the polymer has an MFI before silane grafting in the range 1 to 150, preferably 1 to 80, more preferably 2-20, and for at least one other of which the polymer

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has an MFI before silane grafting in the range 150-2500, preferably 200-800.

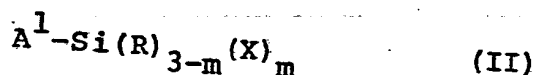
In the SGPs used according to the invention, the silane side chain is conveniently of general formula (I)



wherein A represents an optionally substituted divalent organic radical, preferably an optionally substituted alkylene, alkyleneoxy, alkylene-phenylene, or alkylene-oxy-alkylene chain; X represents a leaving group displaceable by hydrolysis, conveniently a halogen atom (e.g. chlorine) or a group  $R^1O-$  or  $R^1COO-$  where  $R^1$  is a  $C_{1-10}$ , preferably  $C_{1-4}$ , alkyl or alkoxyalkyl group; m is 1, 2 or 3, preferably 2 or 3; and R represents a blocking group not displaceable by hydrolysis, for example a  $C_{1-4}$  alkyl group.

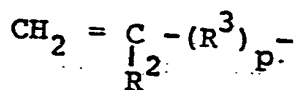
As mentioned above the silane side chains may be present in a monomer which is copolymerised to produce the SGP.

The SGP component for inclusion in the adhesive compositions of the invention may also be prepared by reacting the polymer (or blend thereof) with an unsaturated silane of formula II



(where  $A^1$  represents an ethylenically unsaturated organic group corresponding to the divalent group A in formula I and R, m and X are as defined above) in the presence of a catalyst, conveniently a peroxide catalyst, for example using the reagents and conditions specified in the literature.

In formula II,  $A^1$  conveniently represents a group of formula





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where p is 0 or 1;  $R^2$  represents hydrogen or  $C_{1-4}$  alkyl; and  $R^3$  represents a  $C_{1-10}$  straight, branched or cyclic alkylene group, a phenylene group, a carbonyloxy group, a carbonyloxy( $C_{1-10}$  alkylene) group, a ( $C_{1-10}$  alkylene)carbonyloxy group or a ( $C_{1-10}$  alkylene)carbonyloxy( $C_{1-10}$  alkylene) group, optionally carrying pendant glycidoxy groups.

Such compounds are described by Dart Industries in GB-A-1347426.

Particularly preferably however  $A^1$  represents a  $C_{2-5}$  monoalkenyl group, such as vinyl or allyl, or a ( $C_{2-3}$  alkenyl)carbonyloxy( $C_{2-3}$  alkylene) group, such as a gamma-methacryloxy propyl group, and particularly preferred unsaturated silanes of formula II include vinyl trimethoxy silane, vinyl triethoxy silane and gamma-methacryloxypropyl trimethoxy silane.

Unsaturated silanes of formula II are known or may be prepared by conventional methods.

The silane side chain need only constitute a minor part by weight of the SGP, e.g. up to 20%, generally 0.1-10%, preferably 0.5 to 6% and especially preferably about 4%, and the ratio of unsaturated silane to polymer used in the grafting reaction should be chosen accordingly, or alternatively the weight ratio of monomers where copolymerisation is used.

The catalyst used in the preparation of the SGPs is preferably a free-radical generating compound such as for example benzoyl peroxide, dicumyl peroxide or other catalysts referred to in the literature, e.g. in US-A-3646155. The free radical generator may conveniently be used in a concentration of about 0.01 to 3% relative to the weight of polymer used.

The silane grafting reaction is conveniently effected at a temperature of at least 140°C, preferably between 150°C and 250°C, and may be performed in conventional apparatus such as a Ko-Kneader.

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The SGP component preferably forms up to 99%, conveniently 10-40%, and especially preferably about 30%, of the adhesive composition.

In the adhesive composition of the invention, SGPs having a 3-membered or longer chain linking the silicon atoms with the polymer backbone will result in a cured adhesive having a generally more open structure than that achieved with only a 2-membered linking chain. The open structure may advantageously permit both a high degree of curing and the inclusion of relatively high concentrations of tackifying resin and other components in the uncured adhesive composition. In this way, the viscosity, tack and melting characteristics of the uncured adhesive may be tailored to particular desired levels, for example to permit the use with the new adhesive of conventional hot melt adhesive melting, mixing and application apparatus.

As the catalyst for the SGP hydrolysis and cross-linking, a silanol condensation catalyst may be used. Many such materials are known to the art. Thus suitable catalysts include, for example, metal carboxylates, e.g. dibutyl tin dilaurate, organometallics, e.g. tetrabutyl titanate, organic bases, e.g. ethylamine, and mineral and fatty acids. Several such compounds are identified for example in US-A-3646155. Among suitable condensation catalysts, organotin compounds, such as dibutyl tin dilaurate are preferred. The catalyst, conveniently makes up from 0.005-0.2%, preferably about 0.02%, of the adhesive composition as a whole.

The adhesive composition of the invention conveniently also contains further components selected from: antioxidants; tackifying resins; further polymers; and diluents and modifiers.

The tackifying resin component of the hot melt adhesive composition of the present invention may comprise any suitable resin or resin mixture,

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for example those conventional for hot melt adhesives. The resin or resin mixture should however be selected to achieve the desired balance between compatibility with the SGP and the other components of the adhesive, the melt flow properties of the adhesive as a whole and the specific adhesion to the substrates intended to be bonded with the adhesive. In this respect, suitable tackifying resins may include: aromatic modified resins such as  $\alpha$ -methyl styrene homopolymers or copolymers, e.g. Krystalex F100 ( $\alpha$ -methyl styrene polymer), Krystalex FR75 (a modified  $\alpha$ -methyl styrene copolymer) or Piccotex (a vinyl toluene- $\alpha$ -methyl styrene copolymer), all three available from Hercules Chemical Co.; aliphatic petroleum hydrocarbon resins; styrene-modified hydrocarbon resins; and, particularly preferably, alicyclic hydrocarbon resins, e.g. Escorez 5300 (available from Exxon).

The tackifying resin will conveniently make up from 5 to 40%, preferably 10-40%, and especially preferably about 30%-35%, of the adhesive.

The hot melt adhesive of the invention preferably contains at least one antioxidant. In this respect, conventional adhesives antioxidants, such as butylated hydroxytoluene (BHT) may be used. A preferred antioxidant is pentaerythritol-tetrakis-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate, which is available under the trade name Irganox 1010 from Ciba-Geigy UK Ltd. of Manchester. The antioxidant will generally be present in the adhesive at about 0.1-2.5%, preferably 0.5-1%.

The adhesive system may if desired be formulated as two compositions which are not mixed until the adhesive is melted for application so as to avoid earlier contact between the SGP and the condensation catalyst. Thus according to a further aspect of the invention we provide a hot melt adhesive system comprising a first composition comprising at least

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one SGP as defined above and a second composition comprising a catalyst for the condensation of said SGP, said first and second compositions being packed in separate containers.

The adhesive composition of the invention preferably also comprises a further polymer or polymer mixture. The further polymer or polymer mixture, which should not be cross-linkable under the action of the catalyst, will be selected to achieve, inter alia, a balance between compatibility with the catalyst and the other components of the adhesive and the viscosity and tack characteristics of the adhesive. Since the SGP is based on a polymer deriving from apolar monomers, the further polymers are preferably selected from homo- and copolymers of apolar monomers, such as for example polyethylthene, polypropylene, polybutylene, and SEBS (for example low crystallinity range molecular weight homo-or copolymers, such as that available under the trade name Vestoplast 608 from Huls (UK) Limited of Manchester, or low molecular weight polyethylene, such as polyethylene AC6 or AC8 available from Allied Chemical Corporation International NV SA of Birmingham). Conveniently polymers having MFIs of 1 to 2500, preferably 5-800, more preferably 20-500 and most preferably 150-400 are used. The further polymer conveniently constitutes up to 15%, preferably 1 to 10%, and especially preferably about 5%, of the adhesive of the invention and generally will be present at about half the concentration of the SGP.

The adhesive composition or system may also contain further components such as diluents or modifiers, conveniently as about 5-40%, preferably about 30%, of the total adhesive. These components may serve to regulate the viscosity and setting speed of the adhesive and may be included to enhance the wicking of the adhesive into the substrates

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to be bonded. In this respect, conventional diluents and modifiers for hot melt adhesives, such as waxes (e.g. petroleum waxes such as paraffin waxes or microcrystalline waxes such as Okerin 8981 from Astor Chemicals of West Drayton, Middlesex), hydrogenated animal or vegetable fats (e.g. hydrogenated castor oil or hydrogenated tallow), and synthetic waxes, such as Fischer Tropsch waxes may be used.

Where waxes or low molecular weight polyethylenes are used as diluents, they should conveniently have softening temperatures in the range of 50-120°C. Microcrystalline waxes, Fisher Tropsch waxes and paraffin waxes having softening temperatures in the ranges 65 to 94°C (e.g. 79°C), 110 to 120°C and 54 to 72°C respectively are particularly suitable. A mixture of low molecular weight polyethylene, such as polyethylene AC6 or AC8, and a microcrystalline wax having a softening temperature of about 90°C, such as Micro 549 available from Holmes Chemical Company of Uxbridge, may also be particularly suitable, especially where the polyethylene and the wax constitute about 5 and about 15% by weight respectively of the adhesive.

Where the adhesive is formulated as a two part system, the SGP and the catalyst being separately packaged, the optional components can appear in one or both of the separate compositions; the SGP-containing composition will however preferably contain the antioxidant and the tackifier and the catalyst-containing composition will preferably contain a further polymer; the plasticizers, diluents and modifiers may be in either or both compositions. In a two composition system, the catalyst-containing composition particularly conveniently comprises about 99% of polymer compatible with the SGP (e.g. polyethylene, polypropylene or SEBS) and 1% of a catalyst (e.g. dibutyl tin dilaurate).

Where the adhesive of the invention is formulated

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as a single composition it will advantageously be packaged in water-tight containers, for example aluminium cartridges, which containers advantageously will also include a desiccant, for example a sachet of silica gel at the end of a cartridge for a hot melt adhesive applicator. Thus, according to a further aspect of the invention we provide a hot-melt adhesive applicator cartridge comprising a water-tight container containing therein a desiccant and a hot-melt adhesive composition, said composition comprising an SGP as hereinbefore defined and a catalyst for the condensation thereof.

Besides the components discussed above, it may be desirable to incorporate into the hot melt adhesive a colouring agent, for example a whitener such as titanium dioxide. Such colouring agents are particularly readily dispersed within the hot melt adhesive if introduced as solid dispersions in a polymer compatible with the SGP.

In use, the adhesive of the present invention will be heated to melting, generally to 100-200°C preferably about 110-170°C, mixed (e.g. in a cartridge loaded applicator or by the mixing in a mixer head of the two compositions of a two composition system) and applied to the substrates to be bonded, generally in a film thickness of up to about 3 mm, preferably up to about 1 mm, although this can be achieved by applying a larger amount and scraping off the excess. The adhesive characteristics of the system should be sufficient to maintain a bond between the substrates while the curing of the SGP component by hydrolysis and cross-linking occurs.

For the hydrolysis of the SGP, water is required. In general, the necessary water can be supplied by ambient moisture. However, if desired, the adhesive may contain further components which gradually release moisture into the system, for example fillers with surface-bound moisture or moisture filled

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polymer microspheres such as those sold as paint opacifiers by Rohm and Haas Company under the trade name ROPAQUE OP-62 (see EP-A-119054 of Rohm and Haas).

The adhesive of the invention may be used in most applications where hot melt adhesives have been used and where full bonding strength is not required immediately after the application of the adhesive. The adhesive of the invention is thus particularly suited to use in product assembly (for example in the furniture and automobile industries), packaging and labelling.

Thus according to a further aspect of the invention we provide the use of the adhesive composition and system of the invention in product assembly.

Because of the silane cross-linking reaction, the adhesive of the invention is capable of chemically bonding to the surfaces of certain substrates to produce an enhanced adhesive effect. Thus the adhesive of the present invention is particularly suitable for the bonding of cellulosic and siliceous substrates, for example paper and glass, to non-polar substrates, e.g. plastics such as polypropylene and PTFE.

The SGP and catalyst components in the adhesive of the present invention may be selected to achieve particular desired characteristics, for example rate or controllability of curing, and by varying the monomer make-up and the MFI of the polymer precursor for the SGP, and by utilizing blends of SGPs, the formulation characteristics (such as viscosity, softening point, wetting ability, etc.), for the adhesive may be controlled to give a readily processable material.

In a particularly preferred embodiment of the invention, further organic components, such as for example fillers, tack and viscosity modifiers, plasticizers and colorants can be bonded onto the

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cross-linked lattice produced by curing the silane grafted polymer by using for such components compounds containing, or chemically modified to contain, silanol, alcohol, amine or thiol groups. The use of such compounds is particularly advantageous since although they are unreactive towards the SGP in the adhesive composition before the application of the adhesive, on application they are able to bond to the silanols produced in the hydrolysis reaction and thereafter will be chemically bound into the cured adhesive. In this way where such components are polyfunctional, i.e. contain two or more such groups on each molecule, the components may act as intermediaries in the cross-linking and by becoming part of the cross-linked lattice may modify the physical properties of the cured composition. However even when such components are monofunctional they may bond to the silane grafted polymer so reducing any tendency they may have to leach out of the cured composition even under adverse conditions. In this regard mention may be made in particular of glycerol esters of resins, polyamines, diols, polyethylene glycols, hydroxylated waxes and the like.

The use of such reactive compounds may be particularly advantageous in increasing the thermal stability of the cured composition or where the optional component is capable of discoloring or otherwise damaging the substrate or where loss of the component would cause the adhesive bond to be modified undesirably, e.g. where it would deteriorate.

The following Examples are provided to illustrate the present invention further without limiting the scope of protection sought therefor (all percentages and parts referred to herein are by weight unless otherwise specified):



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Example 1One part adhesive composition

The composition is the admixture of the following components:

SGPP <sup>+</sup>	31.3%
Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
175°F Micro wax (microcrystalline wax)	20.0%
Sasol Wax (Fischer Tropsch wax)	10.0%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%

+ The SGPP is the reaction product of vinyltrimethoxy-silane and polypropylene (Vestoplast 828 available from Huls (UK) Ltd - melt viscosity at 190°C of 28000 mPas) prepared with a silane content of about 5% using the procedure of US-A-3646155.

The composition is homogenized prior to the addition of the catalyst. The catalyst is then mixed in and the composition is filled into aluminium cartridges for a hot melt adhesive applicator. A silica gel sachet is placed in the filled cartridge which is then sealed.

The compositions of Examples 2 to 8 are mixed and filled into containers as for Example 1.

Example 2One part adhesive composition

The composition is the admixture of the following components:

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SGPP <sup>+</sup>	31.3%
Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	30.0%

+ The SGPP is the reaction product of vinyltrimethoxysilane and polypropylene (Vestoplast 828 available from Huls (UK) Ltd - melt viscosity at 190°C of 28000 mPas) prepared with a silane content of about 5% using the procedure of US-A-3646155.

#### Example 3

##### One part adhesive composition

The composition is the admixture of the following components:

SGPE <sup>+</sup>	31.3%
Catalyst/polyethylene blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	30.0%

+ The SGPE is the reaction product of vinyltrimethoxysilane and polyethylene (AC8 available from Allied Corporation - melt viscosity at 140°C of 400 mPas), prepared with a silane content of about 5% using the procedure of US-A-3646155.

#### Example 4

##### One part adhesive composition

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The composition is the admixture of the following components:

SGSEBS <sup>+</sup>	31.3%
Catalyst/SEBS blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	30.0%

+ The SGSEBS is the reaction product of vinyltrimethoxy-silane and SEBS (Kraton G-1650 available from Shell Chemical Co. - Brookfield viscosity in toluene solution at 77°F of 1500 mPas), prepared with a silane content of about 5% using the procedure of US-A-3646155.

#### Example 5

##### One part adhesive composition

The composition is the admixture of the following components:

SGPP <sup>+</sup>	31.3%
Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	30.0%

+ The SGPP is the reaction product of gamma-methacryloxy-propyltrimethoxy silane and polypropylene (Vestoplast

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828), prepared with a silane content of about 7-10% using the procedure of US-A-3646155.

#### Example 6

##### One part adhesive composition

The composition is the admixture of the following components:

SG(PP/PE)	31.3%
Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	30.0%

+ The SG(PP/PE) is the reaction product of vinyltrimethoxysilane and a 50:50 blend of Vestoplast 828 and polyethylene AC8, prepared with a silane content of about 5% using the procedure of US-A-3646155.

#### Example 7

##### One part adhesive composition

The composition is the admixture of the following components:

SGPP <sup>+</sup>	31.3%
Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	30.0%

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+ The SGPP is the reaction product of vinyltri-methoxysilane and an atactic polypropylene (APP grade BPH available from Ceroform Ltd - melt viscosity at 190°C of 10,000 to 15,000 mPas), prepared with a silane content of about 5% using the procedure of US-A-3646155.

#### Example 8

##### One part adhesive composition

The composition is the admixture of the following components:

SGPP <sup>+</sup>	31.3%
Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
Irganox 1010 (antioxidant)	1.0%
Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
Hyvis 30 (polybutene - plasticizer)	10.0%
PEG 400 (polyethyleneglycol)	

+ The SGPP is the reaction product of vinyltrimethoxy-silane and Vestoplast 828, prepared with a silane content of about 5% using the procedure of US-A-3646155.

#### Example 9

##### Two composition adhesive system

The first composition comprises the following components:

SGPP <sup>*</sup>	34%
Wingtack 95 (polyterpene resin)	33%
Okerin 8981 (microcrystalline wax)	32.4%
Irganox 1010 (antioxidant)	0.6%

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\* The SGPP is the reaction product of vestoplast 828 copolymer with vinyltrimethoxy silane, prepared with a silane content of 5% using the procedure of US-A-3646155.

The second composition comprises the following components:

28-400 EVA	99%
Dibutyl tin dilaurate	1%

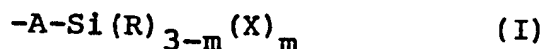
In use, the first and second compositions are melted, mixed in a weight ratio of 98:2 and the mixture is applied to the substrates to be bonded.

If desired, a plasticizer may be incorporated in the two-composition system of Example 9, for example in place of the microcrystalline wax in the first composition. In this regard a 2:1 mixture of plasticizers such as Hyvis 30 (or Wingtack 10) and Benzoflex 9-88 or PEG400 may be used.

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CLAIMS:

1. An adhesive composition applicable in melt form to surfaces to be bonded, said composition comprising
  - (a) at least one silane-modified polymer of apolar monomers,
  - (b) a catalyst for the condensation of said silane-modified polymer, and, optionally,
  - (c) a plasticizer.
2. A composition as claimed in claim 1 containing as said silane-modified polymer a silane-modified olefin homo- or copolymer.
3. A composition as claimed in claim 2 wherein said silane-modified polymer is a silane-modified polymer for which the monomers or comonomers are alpha-olefins.
4. A composition as claimed in either one of claims 1 and 2 wherein said silane-modified polymer is a silane-modified homo- or copolymer the monomers or comonomers of which are selected from ethylene, propylene, but-1-ene, 2-methyl-prop-1-ene and hex-1-ene.
5. A composition as claimed in any one of claims 1 to 4 wherein said silane-modified polymer carries a silane side chain of formula I



wherein A represents an optionally substituted divalent organic radical; X represents a leaving group displaceable by hydrolysis; m is 1, 2 or 3; and R represents a blocking group not displaceable by hydrolysis.

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6. A composition as claimed in claim 5 wherein said silane-modified polymer is a polymer grafted with a silane selected from vinyl trimethoxy silane, vinyl triethoxy silane and gamma-methacryloxypropyl trimethoxy silane.
7. A composition as claimed in any one of claims 1 to 6 wherein the silane side chains on said silane-modified polymers are identical.
8. A composition as claimed in any one of claims 1 to 7 containing from 10 to 40% by weight of said silane-modified polymer relative to the total composition weight.
9. A composition as claimed in any one of claims 1 to 8 containing from 5 to 40% by weight of plasticizer relative to the total composition weight.
10. A composition as claimed in any one of claims 1 to 9 containing a plasticizer selected from polybutene plasticizers, liquid polyterpene plasticizers, liquid hydrocarbon plasticizers and ester-based plasticizers.
11. A composition as claimed in any one of claims 1 to 10 containing 0.005 to 0.2% by weight of said catalyst relative to the total composition weight.
12. A composition as claimed in any one of claims 1 to 11 containing a first and a second said silane-modified polymer, said modified polymers being the products of silane grafting polymers having melt flow indices in the ranges 1 to 20 and 150 to 2500 respectively.
13. A composition as claimed in any one of claims 1 to 12 comprising at least one further component



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selected from antioxidants; tackifying resins; further polymers; and diluents and modifiers.

14. A composition as claimed in any one of claims 1 to 13 further containing a moisture releasing agent.

15. A hot melt adhesive system comprising a first composition comprising at least one silane modified polymer as defined in any one of the preceding claims and a second composition comprising a catalyst for the condensation of said silane-modified polymer, said first and second compositions being packed in separate containers.

16. An adhesive system as claimed in claim 15 wherein at least one of said first and second compositions contains a plasticizer.

17. A hot melt adhesive applicator cartridge comprising a water-tight container containing therein a desiccant and a hot melt adhesive composition as claimed in any one of claims 1 to 14.

17. The use of an adhesive composition or system as claimed in any one of claims 1 to 16 in product assembly.

# INTERNATIONAL SEARCH REPORT

International Application No **PCT/GB 89/00535**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC<sup>4</sup>: C 09 J 3/14, C 08 L 51/06</b>		
<b>II. FIELDS SEARCHED</b>		
Classification System	Minimum Documentation Searched <sup>7</sup>	
<b>IPC<sup>4</sup></b>	<b>Classification Symbols</b> C 09 J, C 08 L, C 08 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>8</sup></b>		
<b>Category<sup>9</sup></b>	<b>Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></b>	<b>Relevant to Claim No.<sup>13</sup></b>
X	EP, A, 0260103 (UNIROYAL) 16 March 1988, see claims 1,12; page 7, lines 39-63	1-7,10,11, 13,14
X	EP, A, 0240044 (SHELL) 7 October 1987, see claims 1,15	1,5-7,9-11
X	EP, A, 0083780 (DAINICHI-NIPPON) 20 July 1983, see page 13, paragraph 3; page 15, paragraph 2	1-8,11,15
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <b>18th August 1989</b>		Date of Mailing of this International Search Report <b>22 SEP 1989</b>
International Searching Authority <b>EUROPEAN PATENT OFFICE</b>		Signature of Authorized Officer <div style="text-align: right; font-size: 1.2em; font-weight: bold;">T.K. WILLIS</div>

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8900535  
SA 28776

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/09/89  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0260103	16-03-88	US-A- 4759992	26-07-88
		US-A- 4767814	30-08-88
		AU-A- 7817787	17-03-88
		JP-A- 63108015	12-05-88
		US-A- 4818789	04-04-89
EP-A- 0240044	07-10-87	US-A- 4783504	08-11-88
		AU-A- 6929387	03-09-87
		JP-A- 62218468	25-09-87
EP-A- 0083780	20-07-83	JP-A- 58189275	04-11-83
		JP-A- 58209524	06-12-83
		JP-A- 58209525	06-12-83
		JP-A- 58116127	11-07-83
		CA-A- 1215528	23-12-86
		US-A- 4726869	23-02-88

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